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(71) Applicant: W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US).

(72) Inventors: AMIRIDIS, Michael, Dimitrios; 12225-K Little Patuxent Parkway, Columbia, MD 21044 (US). KUBSH, Joseph, Edward; 11320 Baritone Court, Silver Spring, MD 20901 (US). PETERS, Alan, Wintrop; 13618 Route 108, Highland, MD 20777 (US). HALLE, Keith, Irwin; 1017 Cordage Walk, Columbia, MD 21044 (US).

(74) Agent: ARTALE, Beverly, J.; W. R. Grace & Co.-Conn., 7379 Route 32, Columbia, MD 21044 (US).

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(54) Title: PT-CONTAINING CATALYST FOR THE REDUCTION OF NITRIC OXIDE BY ORGANIC COMPOUNDS

(57) Abstract

Nitric oxide is reduced in the presence of organic compounds under excess oxygen conditions by passing nitric oxide and an organic compound over a catalyst made of at least one noble metal such as platinum and rhodium on a stable dealuminated Y zeolite from which non framework alumina has been removed. The so treated Y zeolite has a unit cell of less than 24.40 and a mesopore surface area of over 70 $m^2/g$. In a preferred case the treatment of the Y zeolite removes more than 40 % of the number of initial non framework A1 atoms per unit cell. The catalyst is more stable and less susceptible to poisoning by $SO_2$ and water than non-noble metal catalysts.

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# PT-CONTAINING CATALYST FOR THE REDUCTION OF NITRIC OXIDE BY ORGANIC COMPOUNDS.

## Background of the Invention

### 1. Field of the Invention

This invention relates to catalyst for the reduction of nitric oxide by organic compounds under excess oxygen conditions.

### 2. Description of the Previously Published Art

Zeolite catalysts containing fourth period elements for the reduction of NO by hydrocarbons under excess oxygen conditions were first disclosed in 1988 in EP-286967 to Bayer and Volkswagen. The catalyst contains hydrophobic pentasil type zeolites with a Si/Al ratio of at least 15. Such catalyst however, are severely deactivated in the presence of water and sulfur dioxide.

M. Iwamoto and N. Mizuno in Proc. Instn. Mech. Engrs., vol. 207, 23 (1993) in a review article showed that Cu-ZSM-5 is one of the strongest candidates, although it also has durability problems.

Iwamoto et al in Chem. Lett., 2235 (1992) disclose that platinum ion-exchanged ZSM-5 is stable in the presence of oxygen and water vapor. They used mordenite as a comparison zeolite; there is no discussion of using a Y zeolite.

European Patent Application 427,970 to Toyota describes a zeolite catalyst for purifying exhaust gases containing at least one noble metal of platinum (Pt), palladium (Pd) and rhodium (Rh). The zeolite is coated onto a support and the metals are loaded into the zeolite by means of an ion exchange. The zeolite has pores with diameters in the range of 5 to 10 Angstrom units and can

be selected from a group of various zeolites including faujasite with $SiO_2/Al_2O_3$ molar ratios in the range of 10 to 200. There is no discussion using a form of a zeolite where non framework alumina has been removed from the zeolite.

European Patent Application 512,506 to Sumitomo Metal Mining Company relates to a method for removing nitrogen oxides from an exhaust gas with a catalyst containing platinum. The carrier for the Pt is to have a large surface area such as silica, titania, zirconia, aluminum phosphate, silica-alumina, boria-silica-alumina, or zeolite. The catalytic reaction is to take place in an oxidizing atmosphere containing hydrocarbon. The hydrocarbons exemplified are gasoline, kerosene gas oil, or mixtures thereof. None of the examples used a zeolite.

3. Objects of the Invention

It is an object of this invention to provide a novel improved catalyst for the reduction of nitric oxide by organic compounds under excess oxygen conditions.

It is a further object of this invention to reduce nitric oxide with organic compounds under excess oxygen conditions over a catalyst having enhanced stability and durability in the presence of $H_2O$ and $SO_2$.

<u>Summary of the Invention</u>

The use of stable dealuminated Y zeolite which has undergone treatment to remove some of the non framework $Al_2O_3$ as a support for Pt, significantly improves the activity of Pt for the reduction of NO by organic compounds under excess oxygen conditions. Furthermore, this catalyst system is more stable and less susceptible to poisoning by $SO_2$ and $H_2O$ than non-noble metal

catalysts. The treated Y zeolite has a unit cell of less than 24.40 and a mesopore surface area over 70 $m^2/g$. The treatment to remove the non framework alumina preferably removes more than 40% of the number of initial non framework Al atoms per unit cell.

Brief Description of the Drawings

Figure 1 shows the NO conversion at different temperatures over the catalysts and under the conditions described in Example 1.

Figure 2 shows the NO conversation at different temperatures over the catalysts and under the conditions described in Example 2.

Figure 3 shows the NO conversion at different temperatures over the catalysts and under the conditions described in Example 3.

Description of the Preferred Embodiments

Zeolites containing noble metals such as platinum (Pt) and rhodium (Rh) are active catalysts for the reduction of NO by organic compounds under excess oxygen conditions. Pt containing catalysts in particular, have a higher activity than Rh containing catalysts. Both types exhibit a characteristic bell-shaped temperature activity profile with a maximum activity at around 300°C,

Y zeolites have been used in fluid cracking catalysts (FCC) for many years and especially in a dealuminated form (USY) which is thermally stable. We have determined that when the non framework $Al_2O_3$ has been removed from the dealuminated Y zeolite, the resulting zeolite (referred to hereafter as DeY) provides an improved support for a NO conversion catalyst. When Pt, for example, is added to this support, the resulting catalyst has a higher activity than Pt supported on other

conventional alumina supports or other zeolitic supports such as normal Y zeolite, USY which has a high framework silica to alumina ratio, and ZSM-5. The DeY zeolite preferably has a framework molar $SiO_2/Al_2O_3$ ratio of greater than 10, preferably greater than 20 and more preferably greater than 25. Similar improved results are also obtained with a bimetallic Pt-Rh catalyst system.

Various techniques can be used to produce the dealuminated Y zeolite having some of the non framework alumina removed. A preferred procedure is to steam the zeolite and to wash the steamed zeolite with an acidic solution having a pH of about 3.5 or less. This steaming and washing procedure is repeated at least one additional time.

This procedure removes some of the previously existing non framework alumina from the zeolite. This treatment reduces the unit cell to less than 24.40 and it increases the mesopore surface area as measured by the procedure of Johnson in J. Catalysis, **52**, 425-431 (1978) to over 70 $m^2/g$. The unit cell size can preferably be reduced to less than 24.38 and more preferably less than 24.35. The mesopore surface area can preferably be increased to over 85 $m^2/g$. The amount of non framework alumina removed in the zeolite is preferably such that more than 40% of the number of initial non framework Al atoms per unit cell has been removed and more preferably more than 60%.

To measure the mesopore surface area the procedure by Johnson in J. Catalysis, **52**, 425-431 (1978) was used and this is also found in ASTM D 4365-84.

To determine the number of framework aluminum atoms per unit cell, an X-ray diffraction analysis is made. From the unit cell (XRD)

$$\text{no. of Al/uc} = 107\ (\text{unit cell} - 24.23)$$

To determine the number of non framework Al atoms per unit cell, a chemical analysis is made of the total material to determine the amounts of the $SiO_2$ and $Al_2O_3$. The following calculations are made:

$$Si/Al = 0.85\ (\%SiO_2/\%Al_2O_3)$$

$$\text{no. of } Al/uc = 192/(1 + Si/Al)$$

From this total Al per unit cell the amount of the framework Al/uc is subtracted to yield the number of non framework Al/uc.

Another technique to make the product is by the Procedure A described in J. Scherzer in "Dealuminated Faujasite-Type Structures With $SiO_2/Al_2O_3$ Ratios Over 100" in J. Catalysis, **54**, 285-288 (1978).

The source of the noble metals can be several soluble salts of these metals. The metals can be incorporated into the zeolite either by impregnation or by ion-exchange. There are no particular limitations in the methods used, and generally accepted practices of both impregnation and ion-exchange may be employed. The degree of nobel metal coated is preferably between 0.1 and 10% by weight. When smaller than 0.1% a satisfactory catalytic activity can not be obtained. When higher than 10% the process is no more economical due to the cost of the noble metal.

Testing in the presence of $H_2O$ and $SO_2$ shows that the activity of the Pt/DeY system is not significantly affected by the presence of these two gases. On the contrary, our studies show that the presence of these gases significantly decreases the activity of Cu-containing catalysts. Longer durability tests further support the Pt/DeY system stability.

Having described the basic aspects of our invention, the following examples are given to illustrate specific embodiments thereof.

Example 1

This example illustrates the production of a dealuminated Y zeolite with non framework alumina removed.

A 10 kilogram sample of USY (Z14 obtained from Davison Chemical Co.) and having the properties set forth in Table 1 was slurried in 100 liters of water containing 10 kilograms of ammonium sulfate at a temperature of 80°C. 10% sulfuric acid was added to maintain a 2.9 pH for one hour. The sample was then steamed in 100% steam at 1400°C for 3 hours and treated again with the pH 2.9 ammonium sulfate sulfuric acid as described above. The sample prepared by this treatment had a unit cell of 24.43Å and 97% crystallinity. A second steam/calcination and ammonium sulfate/sulfuric acid wash was performed with the results listed in Table 1.

Table 1

| **Properties** | **USY** | **Ex. 1** |
|---|---|---|
| Wt% SiO2 | 71.25 | 94.16 |
| Wt% Al2O3 | 23.961 | 5.804 |
| Wt% Na2O | 4.3 | 0.032 |
| Si/Al Ratio | 2.53 | 13.79 |
| No. Al/unit cell | 54.43 | 12.98 |
| Unit cell, Å | 24.59 | 24.32 |
| No. Framework Al/uc (XRD) | 38.52 | 9.63 |
| No. non Framework Al/uc | 15.91 | 3.35 |
| Micropore SA, $m^2/g$ | 811 | 743 |
| Mesopore SA, $m^2/g$ | 40-50 | 102 |
| % Crystallinity | 93 | 109 |

Example 2

This example illustrates the effect of various supports on the activity of Pt catalysts for the NO reduction by organic compounds.

A series of catalysts was prepared by impregnation of tetraammineplatinum (II) hydroxide ($[Pt(NH_3)_4](OH)_2$) solution onto five different supports:

a. A stable dealuminated Y (DeY) zeolite with non framework alumina removed and having a framework $SiO_2/Al_2O_3$ ratio of about 28 as prepared in Example 1 above.

b. A commercially available USY zeolite (Z14 obtained from Davison Chemical Co.) having a framework $SiO_2/Al_2O_3$ ratio of about 5.0.

c. A ZSM-5 zeolite having $SiO_2/Al_2O_3$ ratio of about 40 and made by Mobil.

d. Y zeolite with a framework $SiO_2/Al_2O_3$ ratio of about 80 and sold under the tradename CBV-780 by PQ Corporation.

e. A conventional lanthana stabilized alumina which is sold under the tradename MI-386 by the Davison Chemical Company.

The catalysts all contained about 1.2% Pt by weight. Following the impregnation, the catalysts were calcined for 1 hour at 550°C in air. They were then ball-milled for 2 hours in a solution containing 3.5% $HNO_3$ based on the weight of the solids in the solution and painted on a metal foil made by Grace Emission Control Products (formerly Camet Co.). Three successive layers were applied to the metal foil (21" length by 1" width), the first being an MI-386 layer without Pt and the next two were the two catalyst layers. The total weight of the washcoat was approximately 1.2 g. Following the application of each layer, the foil-washout combination

was calcined at 500°C in air for 20 minutes. At the end of this process, it was rolled into a cylindrical monolith of 1" diameter by 1" height.

Testing was conducted in a mixture containing 1850 ppm NO, 400 ppm hydrocarbons (3:1 propylene:propane), 1% $O_2$ and balance $N_2$. The reactor was heated in an oven and steady state conversions were determined at 25°C increments in the temperature range of 200-450°C. The results are shown in Figure 1. As it is evident from Figure 1, the Pt/DeY catalyst is the most active catalyst having about 24% maximum conversion. The other three zeolitic supports result in catalysts having maximum conversions of only about 18%. Finally, the non-zeolitic support results in the least active catalyst with a maximum conversion of about 14%.

The use of the stable dealuminated Y zeolite from which the non framework $Al_2O_3$ has been removed as a support results in a higher activity Pt catalyst for the reduction of NO by organic compounds under excess oxygen conditions.

Example 3

This example illustrates the effect of the support on the activity of Pt-Rh catalysts for the NO reduction by organic compounds.

Two catalysts were prepared by impregnation of a co-solution containing tetraammineplatinum (II) hydroxide ($[Pt(NH_3)_4](OH)_2$) and hexaamminerhodium (III) hydroxide ($[Rh(NH_3)_6](OH)_3$) onto two different supports:

a. A stable dealuminated Y (DeY) zeolite with non framework alumina removed and having a framework $SiO_3/Al_2O_3$ ratio of about 28 as prepared in Example 1 above.

b. A conventional lanthana stabilized alumina which is sold under the tradename MI-386 by the Davison Chemical Company.

Cerium oxide (25 wt%) was added to both catalysts which, in their final form, contained about 1.2% Pt and about 0.25% Rh. The preparation of the monoliths and the testing conditions were identical to those described in Example 2. The results are shown in Figure 2. As it is evident from Figure 2, the Pt-Rh/DeY catalysts is more active. It has approximately a 20% maximum conversion compared to a 16% maximum conversion observed over the Pt-Rh/MI-386 catalyst.

The use of the stable dealuminated Y zeolite from which the non framework $Al_2O_3$ has been removed as a support results in a higher activity Pt-Rh catalyst for the reduction of NO by organic compounds under excess oxygen conditions.

## Example 4

This example illustrates that the activity of Pt/DeY catalyst is not significantly affected by the addition of $H_2O$ and $SO_2$ for the NO reduction by organic compounds under excess oxygen conditions whereas a comparison Cu/ZSM-5 catalyst is significantly affected.

A Pt/DeY catalyst containing about 1.2% Pt was prepared as described in Example 2. A Cu/ZSM-5 catalyst containing 5.4% Cu was prepared as described by d'Itri and Sachtler in Catal. Lett., **15**, 289 (1992). The two catalysts were first tested under the conditions described in Example 2. Following this procedure, 10% $H_2O$ and 20 ppm $SO_2$ were added to the reacting gas mixture and new steady state conversions were determined in the same temperature range. The results are shown in Figure 3. As is evident from Figure 3, the addition of $H_2O$ and $SO_2$

has no substantial effect on the activity of Pt/DeY. The activity of Cu-ZSM-5, on the other hand, is significantly decreased in the presence of these two common flue gas components.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

WHAT IS CLAIMED IS:

1. A method of reducing nitric oxide by organic compounds under excess oxygen conditions comprising passing nitric oxide and an organic compound over a catalyst comprising at least one noble metal on a stable dealuminated Y zeolite from which non framework alumina has been removed.

2. A method according to Claim 1, wherein the dealuminated Y zeolite has

a) a unit cell of less than 24.40; and

b) a mesopore surface area of over 70 $m^2/g$.

3. A method according to Claim 2, wherein more than 40% of the number of initial non framework Al atoms per unit cell has been removed.

4. A method according to Claim 3, wherein more than 60% of the number of initial non framework Al atoms per unit cell has been removed.

5. A method according to Claim 2, wherein the unit cell is less than 24.38.

6. A method according to Claim 5, wherein the unit cell is less than 24.35.

7. A method according to Claim 2, wherein the mesopore surface area is over 85 $m^2/g$.

8. A method according to Claim 1, wherein the organic compound is selected from the group consisting of hydrocarbons, alcohols, aldehydes, ketones, organic acids, amines and mixtures thereof.

9. A method according to Claim 1, wherein the noble metal is selected from the group consisting of Pt, Rh and mixtures thereof.

10. A method according to Claim 1, wherein the noble metal is Pt.

11. A method according to Claim 1, wherein the Y zeolite has a framework molar $SiO_2/Al_2O_3$ ratio of greater than 10.

12. A method according to Claim 5, wherein the Y zeolite has a framework molar $SiO_2/Al_2O_3$ ratio of greater than 20.

13. A method according to Claim 5, wherein the Y zeolite has a framework molar $SiO_2/Al_2O_3$ ratio of greater than 25.

14. A method according to Claim 1, wherein the noble metal is present from about 0.2 to 10% by weight.

FIG. I

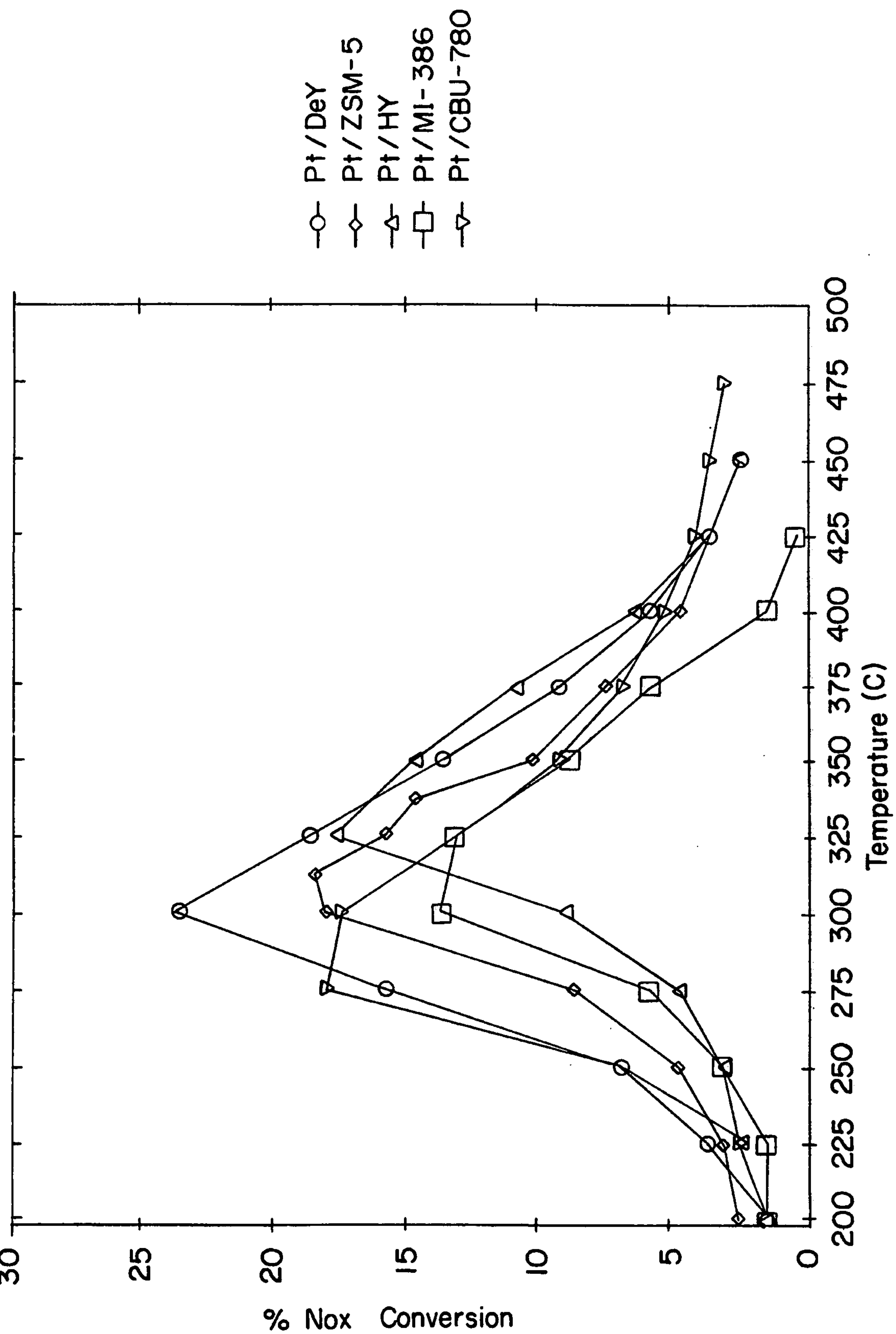

Pt / DeY
Pt / ZSM-5
Pt / HY
Pt / MI-386
Pt / CBU-780
% Nox Conversion
Temperature (C)
0
5
10
15
20
25
30
200
225
250
275
300
325
350
375
400
425
450
475
500

FIG. 2

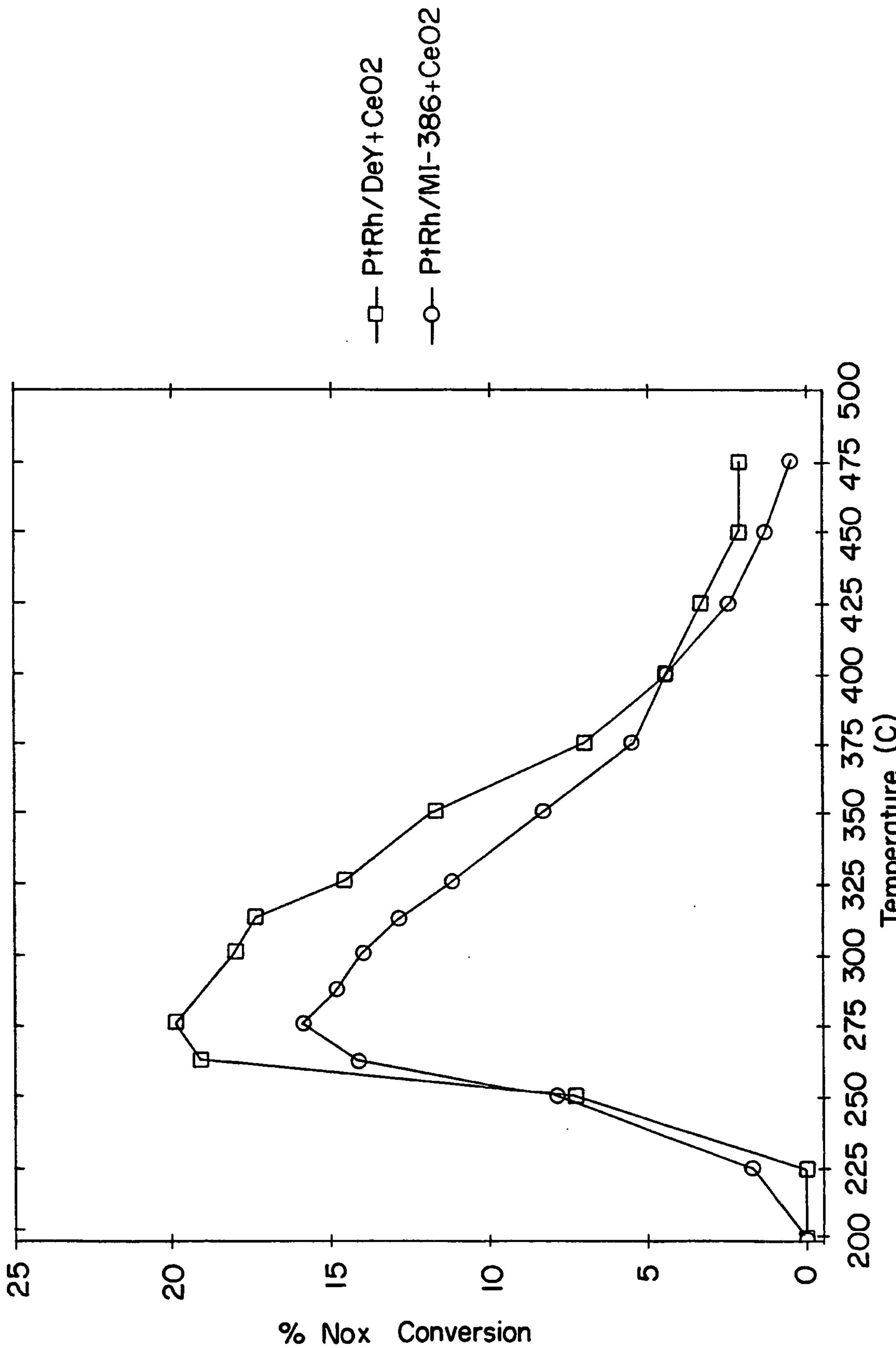
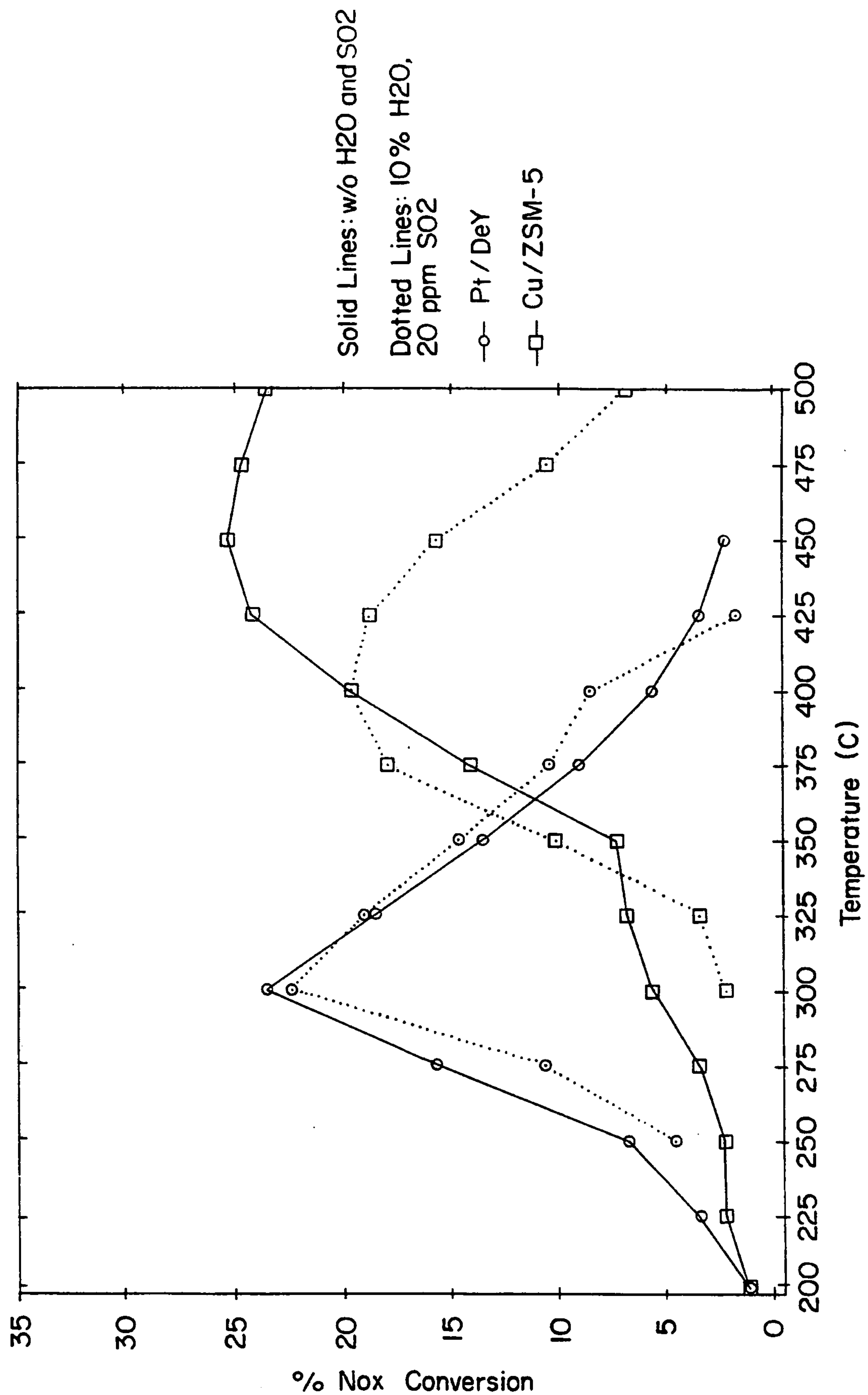

PtRh/DeY+CeO2
PtRh/MI-386+CeO2
% Nox Conversion
0
5
10
15
20
25
Temperature (C)
200
225
250
275
300
325
350
375
400
425
450
475
500

FIG. 3


Solid Lines: w/o H2O and SO2
Dotted Lines: 10% H2O, 20 ppm SO2
Pt/DeY
Cu/ZSM-5
% Nox Conversion
0
5
10
15
20
25
30
35
Temperature (C)
200
225
250
275
300
325
350
375
400
425
450
475
500

# INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 94/13506

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 B01D53/86 B01D53/94 B01J29/12 B01J29/08

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP,A,0 020 799 (UNION CARBIDE CORP.) 7 January 1981<br>see page 5, line 8 - page 13, line 23<br>see page 33, line 18 - line 24; claims 1-15<br>--- | 1,2,5-14 |
| X | EP,A,0 003 818 (UNION CARBIDE COPR.) 5 September 1979<br>see page 3, line 28 - page 12, line 23<br>see page 32, line 18 - line 24; claims 1-15<br>---<br>-/-- | 1,2,5-14 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JOURNAL OF CATALYSIS, vol.54, 1978, NEW YORK, US pages 285 - 288 SCHERZER J. 'Dealuminated Faujasite-Type Structures with SiO2/Al2O3 Ratios over 100' cited in the application | 1-7, 11-13 |
| A | GB,A,2 238 784 (INSTITUTE OF RESEARCH AND INNOVATION (JAPAN)) 12 June 1991 see page 3, line 2 - page 6, line 8; claims 1-4 | 1,8-11 |

1

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Information on patent family members

Inter    ' Application No
PCT/US 94/13506

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|---|---|---|---|---|
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| EP-A-0003818 | 05-09-79 | AU-A- | 4449079 | 30-08-79 |
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| | | DE-A- | 4016688 | 13-06-91 |
| | | FR-A- | 2655565 | 14-06-91 |
| | | US-A- | 5041272 | 20-08-91 |